# TRIATOMIC HYDROGEN AS AN EMITTER OF THE SECONDARY SPECTRUM

STANFORD UNIVERSITY LIBRARY
MAR 16 1928

A DISSERTATION

PRESENTED TO THE
FACULTY OF PRINCETON UNIVERSITY
IN CANDIDACY FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY
CHARLES J. BRASEFIELD

L.C.

STANFORD UNIVERSITY LIBRARIES
WITHDRAWN

3781
P95 B
UNCLASSED
Dissertation

# TRIATOMIC HYDROGEN AS AN EMITTER OF THE SECONDARY SPECTRUM

A DISSERTATION

PRESENTED TO THE
FACULTY OF PRINCETON UNIVERSITY
IN CANDIDACY FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY
CHARLES J. BRASEFIELD

# TRIATOMIC HYDROGEN AS AN EMITTER OF THE SECONDARY SPECTRUM

By Charles J. Brasefield

Abstract

It appears quite probable that some lines in the secondary spectrum of hydrogen may be emitted by an excited $H'_3$ molecule formed by the process $H'_2+H_2 \rightarrow H'_3+H$. Thus Richardson thinks that the question of the rival claims of $H_2$ and $H_3$ to his $H\alpha$, $H\beta$, $H\gamma$, bands is unsettled. Allen and Sandeman have found a band system which they definitely ascribe to $H_3$. An attempt was made to verify these results by correlating the variation in the concentration of $H_3^+$ ions and presumably of $H_3$ excited molecules with the variation in intensity of the lines.

**Variation with pressure of the concentration of $H_3^+$ ions in the positive column of a glow discharge.**—The concentration of $H_3^+$ ions in the positive column of a glow discharge is found to decrease rapidly with pressure and becomes negligible at 0.01 mm. Reasons are given for believing that the recorded concentration of ions is even more truly representative of the conditions in a hydrogen discharge than the results given by the Lenard tubes of Smyth or of Hogness and Lunn.

**Effect of pressure on the relative intensities of the lines of the hydrogen secondary spectrum.**—The relative concentration of $H_3^+$ has no effect on the intensity of the lines of the secondary spectrum with the possible exception of some weak lines such as those of the Allen and Sandeman bands. Evidence is found from Lowe's curves which indicates that the Fulcher lines of Richardson's bands are emitted by the $H_2$ molecule.

## Introduction

IT IS now generally accepted that the secondary spectrum of hydrogen is emitted by a hydrogen molecule. There remains some doubt, however, as to whether the entire spectrum comes from the excitation of diatomic hydrogen or whether its emission may be connected, in part at least, with the formation of triatomic hydrogen.

Numerous investigators have found evidence which leads them to suggest $H_3$ as a possible emitter of a line or a band in the secondary spectrum. From measurements of their half-width, Gehrcke and Lau[1] computed that the carrier of the lines 6326, 6121, 6031, 6018 could be either $H_2$ or $H_3$. Richardson in "Structure Part V"[2] suggested that the probable emitter of his $H\alpha$, $H\beta$, $H\gamma$, etc., bands was neutral $H_2$. However, the predominant strength of the $Q$ branches pointed to an unsymmetrical source. Moreover, the moment of inertia of the normal molecule as calculated from the bands ($4.36\times10^{-41}$ gm cm$^2$) was somewhat larger than that of $H_2$ as calculated from specific heat data. Thus he concluded that the question of the rival claims of $H_2$ and $H_3$ to the bands was unsettled.

Very recently, Allen and Sandeman[3] have found a band system which they ascribe to the $H_3$ molecule, for the emitter of the bands has a very large mo-

[1] Gehrcke and Lau, Preuss. Akad. Wiss. Berlin, Ber. **32,** 453–458 (1922).

[2] Richardson, Proc. Roy. Soc. **A113,** 368 (1926).

[3] Allen and Sandeman, Proc. Roy. Soc. **A114,** 293 (1927).

ment of inertia ($18\times10^{-41}$ gm cm$^2$) which is close to that calculated by Allen for a static model of $H_3$ ($19.33\times10^{-41}$ gm cm$^2$). Further evidence is supplied by the faintness of the system, enhancement in the arc at high pressures, and the peculiar intensity distribution of the lines.

Parallel to these spectroscopic observations we have the results of positive ray analysis which show that $H_3^+$ may be produced in large quantities when hydrogen is ionized.[4] The process involved, of course, is a secondary one, probably that represented by the equation

$$H_2^+ + H_2 \rightarrow H_3^+ + H$$

Let us consider the implications of this result with regard to the emission of radiation. From it we cannot conclude that there is such a thing as a neutral $H_3$ molecule or even an excited $H_3$ molecule. However, if the $H_2^+$ ion is energetically unstable so that it tends to combine with a neutral molecule to form an $H_3^+$ ion, it seems quite possible that an excited $H_2$ molecule, with an electron in an outer orbit, would also be energetically unstable so that it would tend to combine with a neutral molecule to form an excited $H_3$ molecule according to the equation

$$H_2' + H_2 \rightarrow H_3' + H.$$

Of course, in order for such a reaction to be probable it is necessary that the life of the excited $H_2$ molecules be at least as long as the average time between collisions of hydrogen molecules. A simple application of kinetic theory data shows that the time between collisions of molecules in hydrogen at a pressure of 0.01 mm is about $7.6\times10^{-6}$ sec. This is probably longer than the life of the excited hydrogen molecule, so that it seems necessary to postulate either a metastable state in the hydrogen molecule or an abnormally large collision frequency for excited molecules. The first alternative seems very improbable for if such were the case, Smyth[5] and others would have found absorption of lines of the secondary spectrum in the visible region. The second alternative does not seem unreasonable, for the excited molecule is much larger than the neutral molecule and thus would be expected to collide more frequently than the neutral molecule. Such an abnormal collision frequency would shorten the time between collisions for excited molecules to about $10^{-7}$ sec. which is of the right order of magnitude for the life of an excited molecule. Thus it is entirely possible that such a reaction as the one suggested could take place, especially at pressures higher than 0.01 mm. Then radiation arising from the excited $H_3$ molecule or from the recombination of an electron with an $H_3^+$ ion would be expected to show itself in the secondary hydrogn spectrum.

In an endeavor to test these possibilities experimentally or at least to get a correlation between the intensities of various parts of the secondary spectrum and the concentrations of $H_2^+$ and $H_3^+$, simultaneous positive ray and

[4] Dempster, Phil. Mag. **31,** 438–443 (1916); Smyth, Phys. Rev. **25,** 452–468 (1925); Hogness and Lunn, Phys. Rev. **26,** 44–55 (1925).

[5] Private communication.

spectroscopic observations have been made on a discharge in hydrogen under various conditions. The apparatus and results are described below.

## Apparatus and Procedure

In the course of a preliminary investigation,[6] discharge tubes of various shapes and sizes were tried. The discharge tube finally adopted was shaped roughly like a magnified Geissler tube with a tungsten filament cathode and cylindrical nickel anode about 15 inches (38 cm) apart. The anode and cathode were surrounded by 3 inch (7.5 cm) tubing, while between them for about 6 inches (15 cm) was a constriction of 1 inch (2.5 cm) tubing.

The device for analyzing positive ions was connected to the bottom of the discharge tube in the center of the constriction and is shown in Fig. 1.

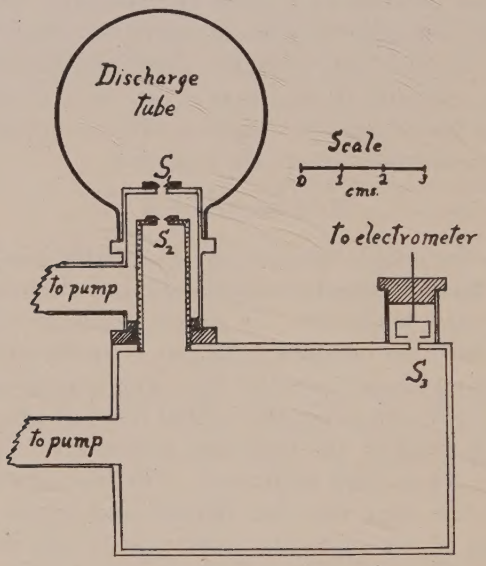


Fig. 1. Apparatus for analyzing positive ions.

The electrode $S_1$ is kept at such a potential that positive ions from the body of the discharge are drawn to it. Entering the slit $S_1$ (0.2 mm wide) with some initial velocity, they are accelerated by the variable field $V$ between $S_1$ and $S_2$ (0.3 mm wide), then bent in a semicircle by the magnetic field, and reach the Faraday cylinder connected to a Compton electrometer. With constant conditions in the discharge tube and constant magnetic field, the ion current reaching the electrometer is observed as a function of the electric field $V$. The resultant curve then gives the relative concentrations of $H_1^+$, $H_2^+$ and $H_3^+$. It was necessary, of course, to surround the discharge tube by several layers of transformer iron so as to protect it from the magnetic field.

Hydrogen was generated by electrolysis of a solution of barium hydroxide and stored over phosphorus pentoxide. To eliminate oxygen produced in the electrolysis, it was passed over platinized asbestos heated to 250°C, and then

[6] Smyth and Brasefield, Proc. Nat. Acad. Sci. **72**, 443 (1926).

over phosphorus pentoxide to remove any water vapor formed in the reaction. Activated charcoal in liquid air was used for purification in preliminary experiments, but then it was found practically impossible to get rid of the comet tail bands of $CO^+$, which appeared at low pressures. The platinized asbestos was found quite satisfactory, as the comet tail bands disappeared and the only other impurity seemed to be the line 4278 which is the head of one of the nitrogen bands. After purification, the hydrogen was stored in two large reservoirs from which it was admitted to the discharge tube through a capillary leak and liquid air trap. A continuous stream of hydrogen was thus provided, the hydrogen being pumped out through the slit $S_1$.

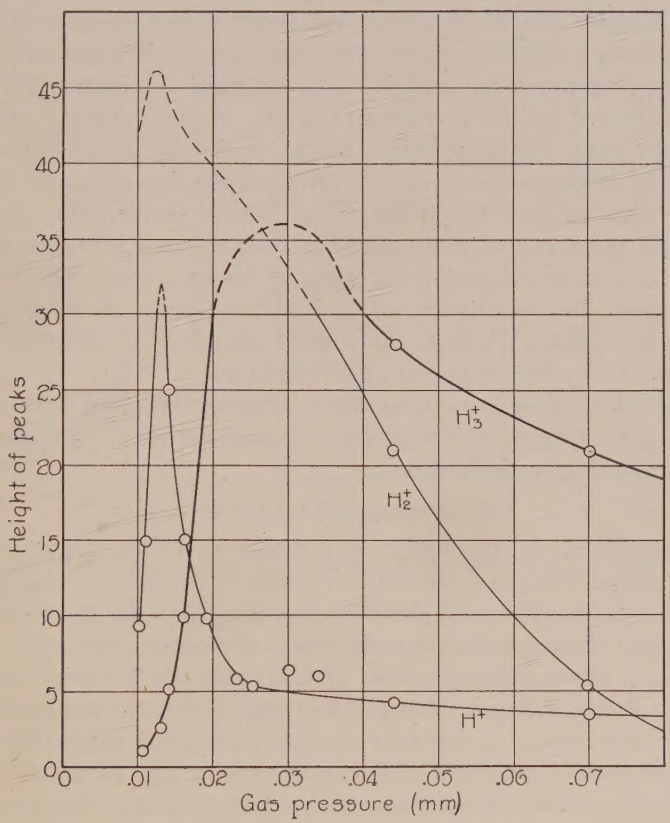


Fig. 2. Variation of the concentration of $H_3^+$, $H_2^+$ and $H^+$ ions with pressure.

## Results

Variations of the relative concentrations of $H_3^+$, $H_2^+$ and $H^+$ ions with pressure were obtained as shown in Fig. 2. Here the potential across the tube was 1000 volts and the current through it 100 milliamperes. The pressures were measured in mms of Hg by a McLeod gauge and the ionic currents in arbitrary units using a Compton electrometer with shunt. At

the time these curves were taken, the interest lay in the lower part of the curves so that the exact form of the curves above the horizontal line at 30 is not known (these readings were off scale). However, a rough idea of the shape was obtained by a method of extrapolation and is indicated by the dotted line. The general decrease in the concentration of $H_3^+$ and $H^+$ above 0.03 mm is probably due to scattering in the positive ray box.

It is of interest to compare these curves with analogous curves obtained by Smyth and by Hogness and Lunn from their study of the products of ionization of hydrogen. The most noticeable difference is in the shape of the $H_3^+$ curve which reaches a maximum and then drops sharply to the pressure axis around 0.01 mm (at 0.01 mm the $H_3^+$ peak had become so small as to be blended with and not distinguishable from the $H_2^+$ peak). The $H_3^+$ curves of Smyth and of Hogness and Lunn point straight at the origin. However, when it is remembered that the $H_3^+$ ion is a secondary product, it is evident that the number of $H_3^+$ ions recorded will depend greatly on the distance traversed by the $H_2^+$ ion in the gas. At first sight, it might appear that this distance would be larger in the present apparatus than in those of Smyth and of Hogness and Lunn. But if all the ions recorded are produced within, or very near to the positive ion sheath surrounding $S_1$, then it is evident that the $H_2^+$ ion will only have to traverse a distance of the order of 1 mm,[7] as compared with a distance of about 1 cm in the other experiments. So that any secondary effect would be expected to disappear at a pressure much greater than in the case of Smyth or of Hogness and Lunn, which agrees fairly well with the observed facts.

It is felt that these curves, at least between 0.01 and 0.03 mm give an accurate representation of the relative concentration of the different kinds of ions in a hydrogen discharge.

## Spectroscopic Observations

Photographs of the discharge were taken on Ilford Rapid Process Panchromatic plates using a constant deviation spectrograph, the slit of which was directed at the region of the discharge immediately above the electrode $S_1$. First, two photographs were obtained of the spectrum, one at 0.01 mm for a six hour exposure and one at 0.20 mm for ten minutes exposure, the potential drop and current through the tube being 1000 volts and 100 milliamperes in each case. In the first case, however, the ratio $H_3^+$ to $H_2^+$ was negligible while in the second case it was very large. Although the general intensity of the secondary spectrum was the same in the two cases, there was a marked change in the intensity of some lines. Professor K. T. Compton suggested that this might possibly be due to a difference in electron energy, for Hughes and Lowe[8] had shown what a marked effect the electron velocity has on the intensity of the lines of the secondary spectrum. With $S_1$ as an

[7] The thickness of the positive ion sheath surrounding $S_1$ was calculated from the equation $i\,d^2 = (4\times10^{-8})\,V^{3/2}$ where $d$ is the thickness of positive ion sheath in cm; $V$ the voltage drop across positive ion sheath; $i$ the positive ion current density at the electrode $S_1$. The results showed that $d = 2.5$ and 1.5 mm at pressures of 0.01 mm and 0.015 mm respectively.

[8] Hughes and Lowe, Phys. Rev. **21,** 297 (1923).

exploring electrode, measurements were made of the mean electron velocity in the two cases. It was found that for a pressure of 0.20 mm the mean electron velocity was about 10 volts while at 0.01 mm pressure the mean electron velocity was nearly 30 volts.

However, at a pressure of 0.015 mm the electron velocity was found to be about 25 volts although the number of $H_3^+$ ions was still five times as large as at 0.01 mm. It was thought that under such conditions the effect of different electron velocities should be small compared to any increase in intensity that might be ascribed to an increase in concentration of $H_3$. Therefore, a photograph was taken at 0.015 mm, an exposure time of one and forty minutes being sufficient to give a plate on which the majority of lines were approximately equal in intensity to corresponding lines on the six hour exposure plate at 0.01 mm.

Microphotometric records were then made of the two plates. When the records were compared it was found that in general the lines on the high

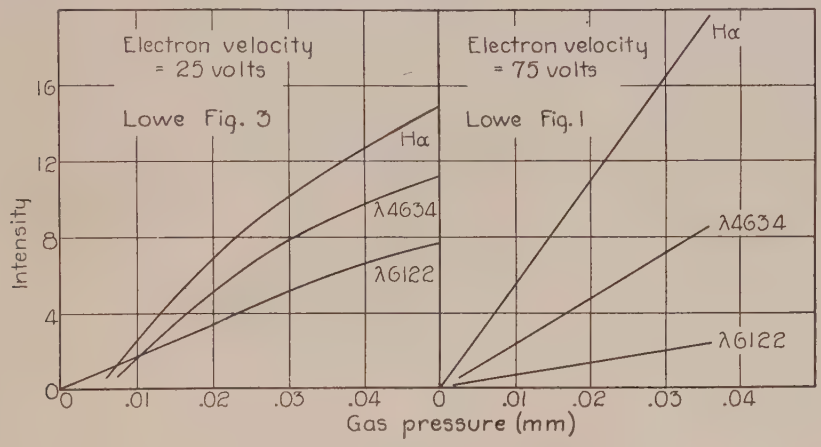


Fig. 3. Lowe's curves of the variation of intensity with pressure of a few secondary lines.

pressure plate were slightly weaker than the corresponding lines on the low pressure plate, except in a few cases. There was evidently a marked enhancement of the Fulcher lines in the red and blue on the high pressure plate. Hence these lines were first provisionally ascribed to $H_3$. The great difficulty, however, was that the Fulcher lines in the green, which according to Richardson's classification are intimately connected with those in the red and blue, were not enhanced at all on the high pressure plate

At this time the writer's attention was directed to a very admirable paper by Lowe[9] in which he has shown the variation of intensity with pressure of the Balmer lines together with a few secondary lines over a great range in electron velocity. Fig. 3 is from his Figs. 1 and 3 and shows his results at 25 and 75 volts for Hα, for λ6122 and for λ4634. Now λ6122 is a red Fulcher line and may be considered typical of that group, in fact, of all the Fulcher

[9] Lowe, Trans. Roy. Soc. Canada **20**, 217 (1926).

lines. Similarly λ4634 is a secondary line not of the Fulcher group but typical of those lines which were of approximately equal intensity in the two photographs discussed above. We are able, therefore, to reconsider the microphotometric records in the light of Lowe's results. Omitting the details of the comparison the conclusion may be stated that the changes in intensity of the Fulcher lines are partially accounted for by the change of electron velocity from 25 to 30 volts and certainly not to be correlated with the five-fold change in the concentration of $H_3^+$ which is definitely a pressure effect.

At first sight it appears that further evidence as to the origin of the lines may be adduced from the shape of Lowe's curves. The intensity versus pressure curves for lines emitted by $H_2$ should go through the origin while curves for lines from secondary sources such as H or $H_3$ should cut the axis of pressure analogously to the $H^+$ and $H_3^+$ curves of Fig. 2. The curve for $H\alpha$ cuts the axis at low voltages and passes through the origin at high voltages and is thus consistent with the belief that excited atomic hydrogen is chiefly due to a secondary effect at low electron speeds and to primary effect at high speeds. However, the curves in Fig. 3 for λ4634 and λ6122 are quite different from each other although we have no other reason to suppose that λ4634 is from a secondary source. The most that can be said with certainty is that the curve for λ6122 (and the other Fulcher lines) is consistent with the idea that they come from $H_2$. As to λ4634, if it is from a secondary source, the positive ray analysis nevertheless shows that its emission is not connected with the formation of $H_3^+$.

There remain to be considered the lines of Allen and Sandeman. Unfortunately most of them are weak and close to other lines so that the microphotometric records give no satisfactory evidence about them. Such of them as were studied by Lowe give intensity vs. pressure curves of shape varying with voltage but suggesting that these lines may actually be of secondary origin.

Our final conclusion, therefore, is that the relative concentration of $H_3^+$ has no effect on the intensity of the lines of the secondary spectrum with the possible exception of some weak lines such as those of the Allen and Sandeman bands.

The writer wishes to thank Professor H. D. Smyth for suggesting the problem and aiding in its development, and Professor K. T. Compton for advise and encouragement during the course of the work. He is also greatly indebted to Dr. Percy Lowe of the Royal Military College, Kingston, Ontario, for much valuable information.

Palmer Physical Laboratory,
Princeton University,
September 24, 1927.

Accepted by the Department of Physics
May, 1927.